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Kinetic-Spectrophotometric Determination of Mn^{II} in Nanograms Based on its Catalytic Effect on Periodate Oxidation of 2-amino-*m*-xylene.

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ABSTRACT

The progress of Mn^{II} catalysed periodate oxidation of 2-amino-*m*-xylene in acetone-water medium was followed by monitoring the increase in the absorbance of reaction intermediate. The main reaction product is 2,6-dimethyl-*p*-benzoquinone. The reaction was found to be first order with respect to catalyst, substrate and oxidant each. The conditions were developed for kinetic-spectrophotometric determination of Mn^{II} in the range 107.88 – 1294.56 ng/ml. Molar extinction coefficient and Sandell's sensitivity for various calibration curves developed are respectively, 57500 to 68100 L. $mol^{-1}.cm^{-1}$ and 1.78 to 2.11 $ng.cm^{-2}$. The characteristics of various calibration curves, percentage recovery, effect of interferrants and correlation coefficient etc have been evaluated. The method is better in terms of cost of analysis and ease of determination as well as involvement of easily available equipments and facilities.

Keywords: Nanogram Estimation, Mn^{II}, periodate ion, 2-amino-*m*-xylene, 2,6-dimethyl-*p*-benzoquinone

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INTRODUCTION

A perusal of literature reveals that many methods that have been reported for determination of Mn^{II} are based on techniques such as titrimetry, spectrophotometry, pulse polarography, differential pulse anodic stripping voltametry chromatography, flame atomic absorption spectroscopy, flow injection stopped flow spectrophotometry and Inductively coupled plasma optical emission spectrometry etc., and involve a complicated pre-treatment of samples, complex operation and use of costly equipments. There are some reports on determination of Mn^{II} based on periodate oxidation of some substrates [1-6]. Mn^{II} catalysed periodate oxidation of aromatic amines has not been explored widely for kinetic-spectrophotometric estimation of Mn^{II} and only a few attempts have been made in this direction [7,8], although there are some reports available in literature related to the Mn^{II} catalysed/ uncatlysed periodate oxidation of aromatic amines [9-21]. In continuation to our kinetic mechanistic studies made on Mn^{II} catalysed periodate oxidation of 2-amino-*m*-xylene [22], a new method developed by us for Mn^{II} estimation based on its catalytic effect on the periodate oxidation of 2-amino-*m*-xylene (XYL), is being reported in present communication.

EXPERIMENTAL

Thiel, Schultz and Koch buffer [23], consisting of different volumes of 0.05 M oxalic acid, 0.02 M boric acid, 0.05 M succinic acid, 0.05 M sodium sulphate and 0.05 M borax, was used for maintaining the pH. Triply distilled water was used for preparation of the solutions. Sodium metaperiodate (Loba Chemie), XYL (Aldrich), acetone (E. Merck), manganese sulphate monohydrate (Aldrich) and all other chemicals of analytical reagent/ guaranteed reagent grade were used after redistillation/ recrystallization. The reaction was studied in a spectrophotometric cell and initiated by adding temperature equilibrated $NaIO_4$ solution of known concentration to the reaction mixture containing the XYL, Mn^{II} and buffer and maintained at the desired temperature ($\pm 0.1^0$C). The progress of the reaction was followed by recording the absorbance on Shimadzu double beam spectrophotometer (UV-1700), at 448 nm, i.e., the λ_{max} of the reaction mixture, during the period in which λ_{max} remained unchanged under experimental conditions. Figure 1, shows the absorption maxima of reaction mixture at different time. Desired temperature was maintained with the help of a high precision in-built thermostatic control.

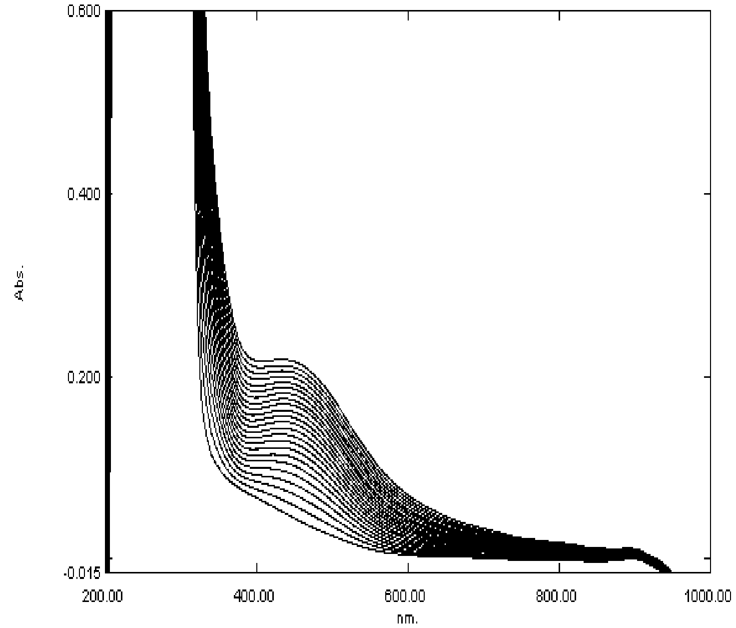

Figure 1: UV-VIS scan of reaction mixture at different time [time interval: 30 sec.]

RESULTS

As already reported by us [22], the reaction was found to be first order in each reactant and catalyst with 1 mol of XYL reacting with 2 moles of periodate in initial stage of reaction and 2,6-dimethyl-*p*-benzoquinone being the main product of oxidation. Rate-pH profile showed a maximum at pH=6.0. Increase in dielectric constant of the medium increased the rate of reaction. An attempt was made to make use of the kinetic studies to work out the best suitable conditions leading to the kinetic-spectrophotometric estimation of Mn^{II} in nanograms while it catalyses the XYL–periodate redox system in acetone-water medium. The studies were made by taking oxidant in excess.

The conditions worked out for estimation of Mn^{II}

Following are the finally worked out conditions for running the kinetic sets for the purpose of determination of Mn^{II} in mixed (acetone-water) medium based upon the periodate oxidation of aniline: [XYL] = 0.001 M; [$NaIO_4$] = 0.01 M; Acetone = 10% (v/v); pH = 6.5; λ_{max} = 448 nm; Temp.= 35 ± 0.1°C. The method developed was suitable for estimation of Mn^{II} in the range 107.88 ng/ml to 1294.56 ng/ml.

Preparation of calibration curves

A definite volume of stock solution of XYL in acetone was mixed with calculated volume of the stock solution of Mn^{II}, acetone and water and stirred a little with the help of the pipette. This mixture and stock solution of $NaIO_4$ were then clamped in a thermostat at 35 ± 0.1°C. After 30 minutes, a required amount of the periodate solution was added to the mixture and stirred to start the reaction. All additions were made in amounts calculated for maintaining the concentrations of different reagents as mentioned above. Different sets were prepared in a similar manner varying the [Mn^{II}]. The reaction mixture was transferred to the cuvette of double beam spectrophotometer immediately after start of reaction. The desired temperature was maintained in spectrophotometer cell also. The absorbance was recorded after repeated intervals of 40 seconds. The absorbance vs time plots were then made for different sets. The initial rates [$(dA/dt)_{40}$] were evaluated after 40 seconds from the start of the reaction by applying plane mirror method on the absorbance vs time plots. The pseudo first order rate constants (k_{obs}) were found by Guggenheim's method. Using the method of least squares, linear calibration curves were obtained. Type 'A', type 'B', type 'C', type 'D', type 'E' and type 'F' plots were obtained in terms of A_{160} or A_{200} or A_{240} or A_{280} or initial rate or k_{obs} vs [Mn^{II}] plots respectively (Figure 2, 3). Where A_{160} or A_{200} or A_{240} and A_{280} are the absorbance values after 160, 200, 240 and 280 seconds from the start of reaction respectively.

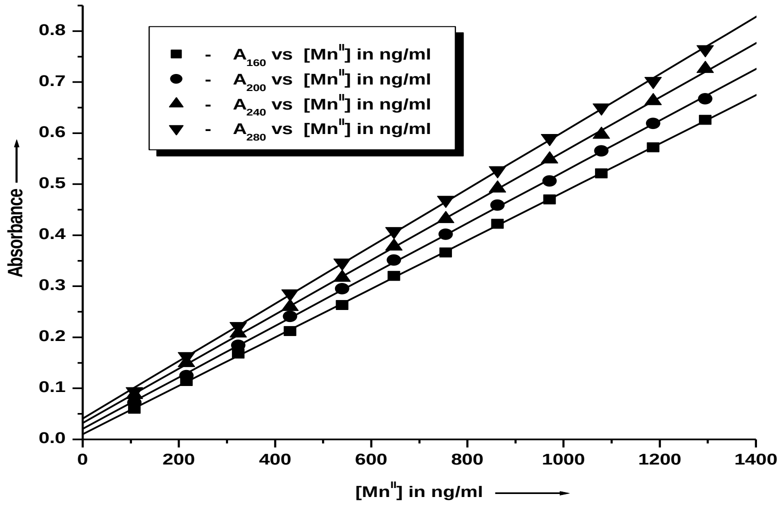

Figure 2: Calibration curves in term of Absorbance vs [Mn^{II}] plots.
[$NaIO_4$] = 0.01 M; [2-XYL] = 0.001 M; pH = 6.5, acetone = 5.0%; Temp = 35 ± 0.1ºC; λ_{max} = 448 nm

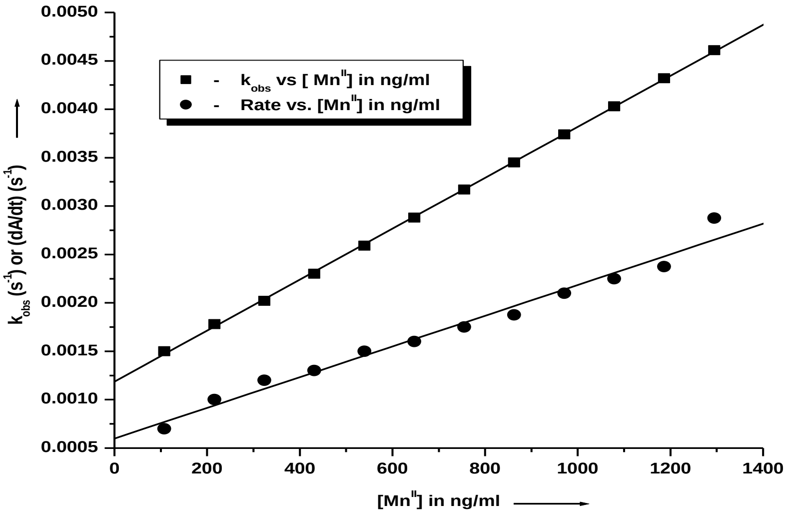

Figure 3: Calibration curves in term of rate constant or Initial rate vs [Mn^{II}] plots
[$NaIO_4$] = 0.01 M; [2-XYL] = 0.001 M; pH = 6.5 Acetone = 5.0 %; Temp = 35 ± 0.1º C; λ_{max} = 448 nm

Table 1: Characteristics of various types of calibration curves for the proposed method

$[XYL] \times 10^3 = 1.0$ M; $[NaIO_4] \times 10^2 = 1.0$ M; pH = 6.5;

Acetone = 10.0% (v/v); Temp = 35 ± 0.1°C; $\lambda_{max} = 448$ nm;

Parameter	'A' plot	'B' plot	'C' plot	'D' plot	'F' plot	'G' Plot
Beer's law limits (ng/ml)	107.88-1294.56	107.88-1294.56	107.88-1294.56	107.88-1294.56	107.88-1294.56	107.88-1294.56
Molar absorptivity $\times 10^{-4}$ (L $mol^{-1} cm^{-1}$)	5.75	6.10	6.44	6.81	---	---
Sandell's sensitivity (ng cm^{-2})	2.11	1.99	1.88	1.78	---	---
Slope $\times 10^4$ absorbance units ng^{-1} cm^3(from regression equation)	4.74	5.03	5.31	5.62	0.0158	0.026
Intercept $\times 10^2$ (abs units) (from regression equation)	1.03	2.09	3.23	4.09	0.059	0.119
Correlation coefficient (r)	0.9999	0.9997	0.9990	0.9996	0.9886	0.9994
Coefficient of determination (r^2)	0.9998	0.9994	0.9980	0.9992	0.9773	0.9988
't' (at 0.01 significance level)	6.4376	6.615	6.893	6.893	9.3608	10.026
Relative Standard Deviation (%) (for six determinations)	0.1070	0.1081	0.2140	0.0952	0.139	0.1156

Table 3 :Comparison with reported methods

Parameter	I[26]	II[8]	III[2]	IV[3]	V[5]	VI[7]	VII[27]	VIII[28]	IX[29]	X[30]	XI*
Beer's law limits (ng cm^{-3})	1000 – 25000	--	740 – 10320	0.05 – 5.0	0.08– 4.0	1-120	0.00 – 3520	5 –50	5 – 50	32- 200	107.88-1294.56
Molar absorptivity x10 $^{-3}$ (L mol^{-1} cm $^{-1}$)	--	--	4.972	--		99 – 165	5.84 – 7.24	54.945	197. 8	79.2- 180	57.5-68.1
Sandell's sensitivity (ng cm^{-2})	50	1x10^{4}	11	0.015	0.025	0.333 – 0.556	7.3 – 9.2	1.0	0.278	0.306- 0.694	1.78-2.11
Correlation coefficient (r)	--	--	--	--	0.998	0.998 – 1.000	0.998 - 0.999	0.9333-1.003	0.999 - 1.0018	0.9951-0.9987	0.9886-0.9999
Coefficient of determination (r^{2})	--	-	--	--	0.996	0.9996–1.000	0.996 - 0.9984	0.870 - 1.006	0.998 - 1.0036	0.9902-0.9974	0.9773-0.9998
't' (at 0.01 significance level)	--	--	--	--		--	--	--	--	6.793-8.02	6.4376-10.026
Relative standard deviation (%)(From 6 determinations)	--	--	0.73 – 1.4	--	2.7	0.353 – 0.885	0.27 – 0.50	1.509	1.093	--	0.107-0.214
% error	--	--	--	--	1.7 – 3.3	0.37–0.929	0.37 – 0.524	--	--	--	--
Standard deviation (%) (From six determinations)	--	--	--	--	--	--	--	--	--	0.506-1.655	--
% Recovery	--	--	--	--	---	--	--	--	--	99.1-100.0	98.93-99.96

I, II, III --- XI are the numbers assigned to other reported methods

* Present method 9For different type of calibration curves developed)

Note: Detection limits are also available for a few reported methods as 0.014 ng/ml[31], 0.05 ng /ml [32], 0.01 ng /ml (by using flow injection method)[33].

Table 2: Values shown are calculated from calibration curves and are mean of n = 6 in each case.

Concentration	Added (ng/ml)	Detected (ng/ml)	Recovery
A	539.4	538.47	99.94
B	539.4	538.40	99.96
C	539.4	538.39	99.94
D	539.4	537.4	99.87
E(Rate)	539.4	538.10	99.91
F(k_{obs})	539.4	538.32	98.93

Validity of Beer's law and other characteristics of the method

The range of [Mn^{II}] in which the Beer's law is obeyed, molar absorptivity, Sandell's sensitivity, correlation coefficient and the coefficient of determination, value of 't' (at 0.01 significance level) and relative standard deviation for various calibration curves are given in table-1. Some of the characteristics of calibration curves can be presented in the form of equations of straight line as follows:

$$A_{160} = 1.03 \times 10^{-2} + 4.74 \times 10^{-4}\ [Mn^{II}] \qquad \text{-----(1)}$$
$$A_{200} = 2.09 \times 10^{-2} + 5.03 \times 10^{-4}\ [Mn^{II}] \qquad \text{-----(2)}$$
$$A_{240} = 3.23 \times 10^{-2} + 5.31 \times 10^{-4}\ [Mn^{II}] \qquad \text{-----(3)}$$
$$A_{280} = 4.09 \times 10^{-2} + 5.62 \times 10^{-4}\ [Mn^{II}] \qquad \text{-----(4)}$$
$$(dA/dt)_{40} = 0.06 \times 10^{-2} + 0.016 \times 10^{-4}\ [Mn^{II}] \qquad \text{-----(5)}$$
$$k_1 = 0.12 \times 10^{-2} + 0.026 \times 10^{-4}\ [Mn^{II}] \qquad \text{-----(6)}$$

In Eq. (5), the values of intercepts and slope are in absorbance units s^{-1} and absorbance unit s^{-1} ng^{-1} ml respectively. These are in sec^{-1} and sec^{-1} ng^{-1} ml respectively for Eq. (6). The [Mn^{II}] are in ng/ml.

Effect of interferrants

The method is not applicable in presence of most of the aromatic amines/ anilines. The method may be used in presence of the ions like Na^+, K^+, NO_2^-, ClO_4^{-2}, NO_3^-, and SO_4^{-2} as they do not interfere in present case. However, the metals like Ag, As, B, Co, Cd, Cr, Cu, Fe, Hg, Mo, Ni, Pb, Sb, Se, U, and Zn are expected to interfere in this method. Therefore, a pretreatment is required for separating/ precipitating/ masking these ions before undertaking the proposed method. For this purpose, H_2S may be passed in presence of 0.3 M H^+ solution, followed by filtration and boiling off H_2S. After it, a dilute alkaline solution of α-nitroso-β-naphthol should be added and again the solution should be filtered [24]. Thereafter, the solution should be neutralized and the present method be applied. Fe may be removed by precipitation using basic formate method [2,25]. In absence of the above given interferrants, the proposed method may successfully be used for the determination of nanogram quantities of Mn^{II} in water samples.

Procedure for estimation of Mn^{II}

[Mn^{II}] may be determined in aqueous solutions and water samples by mixing the sample with calculated quantity of XYL and acetone and starting the reaction by adding

$NaIO_4$ followed by noting the absorbance of reaction mixture at different desired times as described above, or evaluating initial rate in terms of $(dA/dt)_{40}$ by plane mirror method or evaluating k_{obs} by Guggenheim's method as discussed above. After it, different calibration curves may be used for determination of $[Mn^{II}]$ in ng/ml.

The proposed methods were tested for many water samples containing known amounts of Mn^{II} in the range of the detection limits reported above. The results were found to be reproducible with reasonable standard deviation and low range of errors as calculated from six determinations (table-1, 2). Various characteristics of the calibration curves indicate reasonable sensitivity, molar absorptivity, percentage recovery, and correlation in the range of $[Mn^{II}]$ 107.88 ng/ml to 1294.56 ng/ml. It is clear that method is very well suited to estimation of Mn^{II} in trace amounts. The detection limit in terms of sandell's sensitivity is 1.78–2.11 ng cm^{-2}, which is reasonably good.

DISCUSSION

Molar absorptivity is in the range 57500 to 148243 L mol^{-1} cm^{-1}. Value of Sandell's sensitivity suggests that a change in absorbance by 0.001 unit is expected on changing the concentration of Mn^{II} by 1.78-2.11 ng/ml. The correlation coefficient (r) is in the range 0.9886 to 0.9999 which indicates the high precision involved in the determination and almost perfect correlation of the data. The value of coefficient of determination (r^2) suggests that 97.73% to 99.98% change in the value of absorbance or $(dA/dt)_i$ or k_1 is caused by Mn^{II} and the rest 0.02% to 2.27% is the effect of unknown factors. The value of 't' as calculated for the calibration curves, are in the range 6.4376 to 10.026 which are much higher than the tabulated critical value at 1% significance level. This suggests that there are less than 1% chances of error in drawing conclusions. The standard deviation is within reasonable limits. Percentage recovery on the basis of six parellel determinations is 98.93% to 99.96%.

A comparison of these methods for estimation of Mn^{II} with the other reported methods based on other reactions and using high cost equipments coupled with lengthy pretreatment of samples is given in the table-3 which includes the characteristics of other reported methods. Although lower detection limits are available for some of the reported methods involving/ not involving periodate oxidations, these methods require rarely available facilities like flow injection method. Method reported by Mutaftchiev [3,5] involves low detection limits in the range 0.015 to 0.025 ng/ ml. However, the pre-treatment like complexation etc makes this method more complicated than the method being proposed by us. In general, the proposed method is fairly suitable for estimation of Mn^{II} at nanogram level [26-33].

The methods developed by us are cost effective and involve the use of simple equipments and chemicals that are generally expected to be available in small centers of research or laboratories. The range in which Beer's law is being obeyed, molar absorptivity, Sandell's sensitivity, detection limits, reproducibility of results are good enough to make these methods competent with other reported methods. These methods are better than some of the previously reported methods in terms of the characteristics of calibration curves and the ease of the procedure involved. Further these methods are simple and less time consuming in comparison to the other available methods for estimation of Mn^{II} in aqueous/ mixed media, as no pretreatment of the samples etc are involved except in cases where some rare interferrants are present as already discussed.

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